Structural and Electronic Variation in Selenium Nanoencapsulates in Zeolites

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The Inquiry

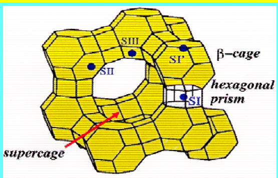
Confinement of semiconductors on length scales below the quantum size limit has the effect of widening the band gap.

The energy levels ultimately transform from a band structure to a discrete level structure.

Nanoporous zeolites with sub-nanometre pore sizes may serve as confinement matrices for semiconductor nanoencapsulate composites.

The structures and electronic band gap properties of selenium encapsulated in a series of zeolites with the faujasite-type structure and a variety of charge-balancing cations have been investigated.

In host matrices with invariant pore size, does the zeolite composition affect the structure and electronic band gap properties of the selenium nanoencapsulate?



Y zeolite cage structure (FAU)

Unit cell composition: $M_{57}(AlO_2)_{57}(SiO_2)_{135}$
(with anionic framework)
Pore diameter = 7.5 Å
Cage diameter ≈ 13 Å

Cation siting

- Trivalent rare earth ions exclusively in ß-cages (SI′)
  Nd^{3+}, La^{3+}
- Divalent cations in hexagonal prisms, ß-cages, and supercages (SI, SI′, SII)
  Ca^{2+}, Sr^{2+}, Cu^{2+}
- Monovalent cations in hexagonal prisms, ß-cages, and supercages (SI, SI′, SII, SIII)
  Rb^{+}, Cs^{+}

Crystalline bulk selenium polymorphs

Trigonal -- chain structure

Monoclinic -- 8-ring molecular structure

Rhombohedral -- 6-ring molecular structure

Selenium also exhibits an amorphous bulk structure, believed to contain polymeric chains and a distribution of rings, with a band gap of 2.05 eV

Nanocomposite formulation

- Zeolite modified by solution ion exchange
- Ion-exchanged zeolite vacuum dehydrated and calcined at 773 K
- Selenium vapor adsorbed at temperatures above 523 K

Experimental studies

- Neutron powder diffraction - structure determination using Rietveld refinement
- Anomalous x-ray scattering - structure determination using pair correlation function of selected element
- Raman scattering - vibrational structure
- Diffuse reflectance uv/visible spectroscopy - electronic structure

Complementary ab initio quantum chemical calculations

[L. A. Curtiss]

- Molecular Se_n clusters and cation-cluster complexes - structures
- Molecular Se_n clusters and cation-cluster complexes - vibrations

Selenium in Y zeolites

Nd-Y and La-Y
- predominantly single Se chains; no Se-cation interaction
- photofragmentation produces Se_2^- radical anions

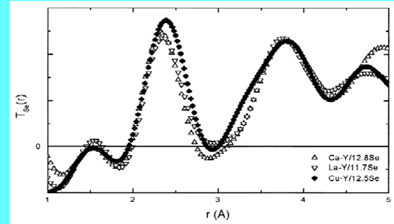
Ca-Y and Sr-Y
- predominantly Se_8 rings; weak Se-cation interaction
- band gap ≈ 2.77 eV, highly blue shifted
- greater chemical stability than Se/La-Y
- photofragmentation produces neutral Se_3 molecules

Rb-Y and Cs-Y
- predominantly Se rings (?); Se-cation interaction (?)

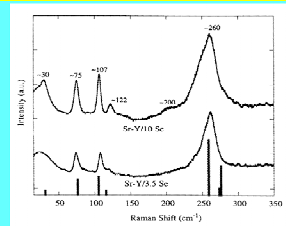
Cu-Y
- predominantly single Se chains, highly disordered
- Se-cation interaction with charge transfer
- band gap ≈ 2.09 eV -- small, due to states created in the gap

The Verdict

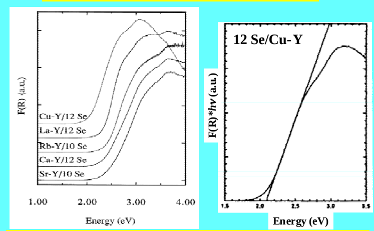
The structure, electronic properties, and chemical stability of selenium encapsulated in Y-type zeolites are significantly influenced by the charge-balancing cations present. Thus, the size of the confining pore is only one of the determining factors in the properties of the selenium /zeolite composite. The reduction of the band gap resulting from charge transfer in Se/Cu-Y suggests that other transition metal charge-balancing cations could be found that would make the gap smaller than that in amorphous bulk selenium. This is contrary to the usual consequence of widening the band gap in semiconductors by constraining the particle size below the quantum size limit.



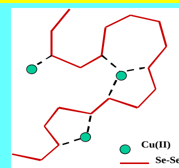
Anomalous x-ray scattering
Comparison of selenium pair correlation functions in Ca-Y, La-Y and Cu-Y zeolites



Raman scattering
Vibrations of Se_8 rings in Sr-Y zeolite



Diffuse reflectance uv/visible spectroscopy
(a) Comparison of selenium optical absorption in Sr-Y, Ca-Y, Rb-Y, La-Y and Cu-Y zeolites
(b) Band gap determination for Se/Cu-Y zeolite



Schematic illustration of strongly disordered Se_n chains with interacting Cu^{2+} ions in Se/Cu-Y

Future

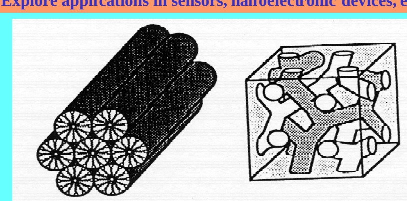
Mesoporous material composites

Nanoencapsulation and Nanocomposites -- Prospects

Host materials
- Ordered mesoporous materials with 2 - 30 nm pores, e.g.,
-- Silicas
-- Semiconductors
-- Metals
-- Magnetic materials
- Silica nanobubbles

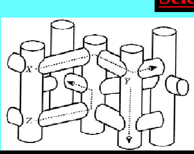
Encapsulates
-- Semiconductors
-- Metals
-- Nanocluster catalysts
-- Magnetic nanoparticles
-- Biomolecules

- Study effects of confinement and interaction
- Organize ordered arrays
- Explore applications in sensors, nanoelectronic devices, etc.



2-D hexagonal and bicontinuous cubic mesoporous structures

Selenium encapsulated in Silicalite



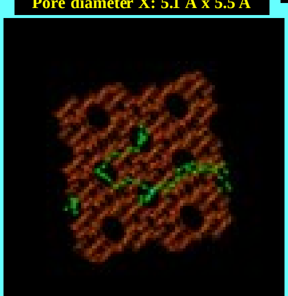
Channel structure of Silicalite
Unit cell composition: $(SiO_2)_{96}$
(with neutral framework)
Pore diameter Y: 5.3 Å x 5.6 Å
Pore diameter X: 5.1 Å x 5.5 Å

Complementary theoretical and simulation studies

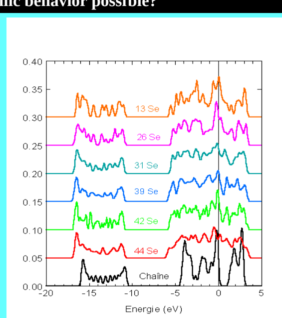
[C. Bichara (CNRS, Marseille) and R. Pellenq (CNRS, Orléans)]

- Grand canonical Monte Carlo calculations
  - Se adsorption isotherm
  - structure of Se encapsulate
- Band structure calculations (tight binding)
  - electronic structure of Se encapsulate in silicalite

-- Is metallic behavior possible?



Structure of Se in Silicalite
(simulation of 73 atoms in 12 unit cells)



Band structure of Se/silicalite
as a function of unit cell loading

References

• A. Goldbach et al., J. Chem. Phys., *in press*; • A. Goldbach et al., Chem. Commun. *1999*, 997; • P. Armand et al., Phys. Rev. Lett. *79*, 2061 (1997);
• A. Goldbach et al., Chem. Phys. Lett. *281*, 69 (1997); • A. Goldbach et al., J. Phys. Chem. B, *101*, 330 (1997); • A. Goldbach et al., J. Am. Chem. Soc., *118*, 2004 (1996)

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